

## MEMO

## ROHM &amp; HAAS COMPANY

Date October 1, 1965

Mr. C. W. Whitmoyer ✓

From C. L. Levesque

cc:

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Dr. Butterbaugh  
Dr. McKeever  
Dr. RJ Myers  
Dr. Nemec  
Mr. Prizer

Received 10 1 1965  
DATE STAMP

Subject:

Arsenilic Acid Process

Attached is a copy of Laboratory 28's write-up of the projected Semi-Works trials. You will note that they have gone back to the 5.5:1 mole ratio rather than the 3.5. The reason for this is some indication that less arsenious acid is formed during recycle with this ratio. In addition, it was felt that first trials should stick to the Whitmoyer conditions as closely as possible. I believe that later work will investigate the 3.5:1 mole ratio.

  
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CLL:ej

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#28-65-97

Bridesburg, September 24, 1965

MEMORANDUM

TO: Mr. C. J. Prizer

FROM: Dr. H. Raterink, Mr. S. Wise, and Mr. D. Nicodemus

SUBJECT: Arsanilic Acid

Because of the waste arsenic disposal problem existing in the current Whitmoyer arsanilic acid process, Laboratory 28 has developed an improved process which allows recovery and reuse of most of the arsenic residues not converted to arsanilic acid. The procedure has been demonstrated in several series through 4 or 5 recycles. In addition, on a preliminary basis, the process appears to have an economic advantage over the present procedure. The work has progressed to the point where demonstration on a larger scale is desirable and an appropriation has been granted for this purpose. Herein is outlined a tentative Semi-Works procedure which incorporates the best laboratory conditions. The number of recycles desired, and perhaps other slight variations in operating conditions, will be established as the work in the laboratory and pilot plant progresses. Any specific immediate data or changes in the procedure described in this report which are desired for plant operation should be suggested as soon as possible by the Development Engineering Group at Bristol or by others concerned with this development.

Briefly, the process is as follows: (1) React arsenic acid with excess aniline (5.5/1 mole ratio) at 160-165°C. for 2 hours; (2) Part of the unreacted aniline is stripped off under reduced pressure (30 mm. Hg); (3) Part of the remaining aniline salt is split with steam and the aniline removed by distillation; (4) The resulting arsanilic acid solution is carbon-treated; (5) The arsanilic acid is crystallized from the carbon-treated solution by cooling and the resulting filter cake is water washed to remove impurities; (6) Mother liquor (filtrate) and wash water is concentrated to approximately 60% solids under vacuum (90 mm. Hg) and the residue, containing both arsenic and aniline (combined as salt), is recycled together with recovered aniline to the succeeding run.

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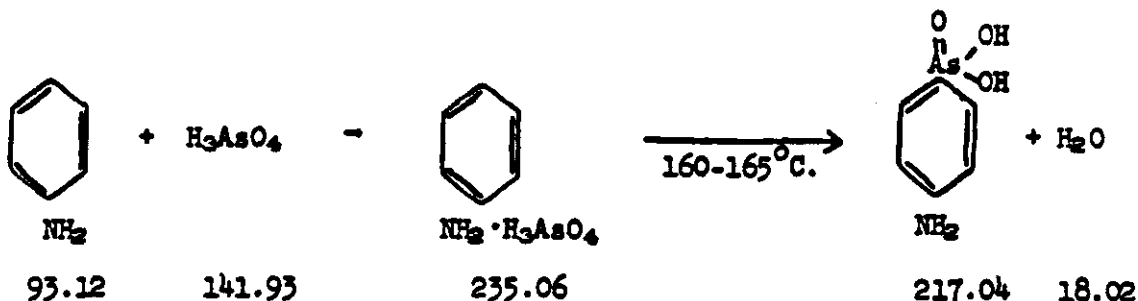
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Arsenic conversion to arsanilic acid is about 26% which is equivalent to the conversion obtained using the present process. In the latter case arsenic residues are contaminated with inorganic salts which makes recycle impracticable.

### I. Chemistry



### II. Equipment

Because of the toxic nature of aniline and arsenic compounds, the reactions will be performed in the Semi-Works Toxic Area. The equipment in this area will be modified to simulate the proposed plant as nearly as possible as shown in Figure 1.

#### A. Reactor

Unit 117, a 100-gallon, 316-stainless steel kettle with a condenser, receiver, vacuum source, and separator pot are to be used for the reaction step. At the completion of the reaction and vacuum stripping, as much hot water as possible will be added to Unit 117 with the remaining water of solution for the arsanilic acid to be added continuously to the transfer line leading to the steam stripper. The reactor effluent will be pumped continuously to the packed column on Unit 116 for steam stripping.

#### B. Steam Stripping Unit

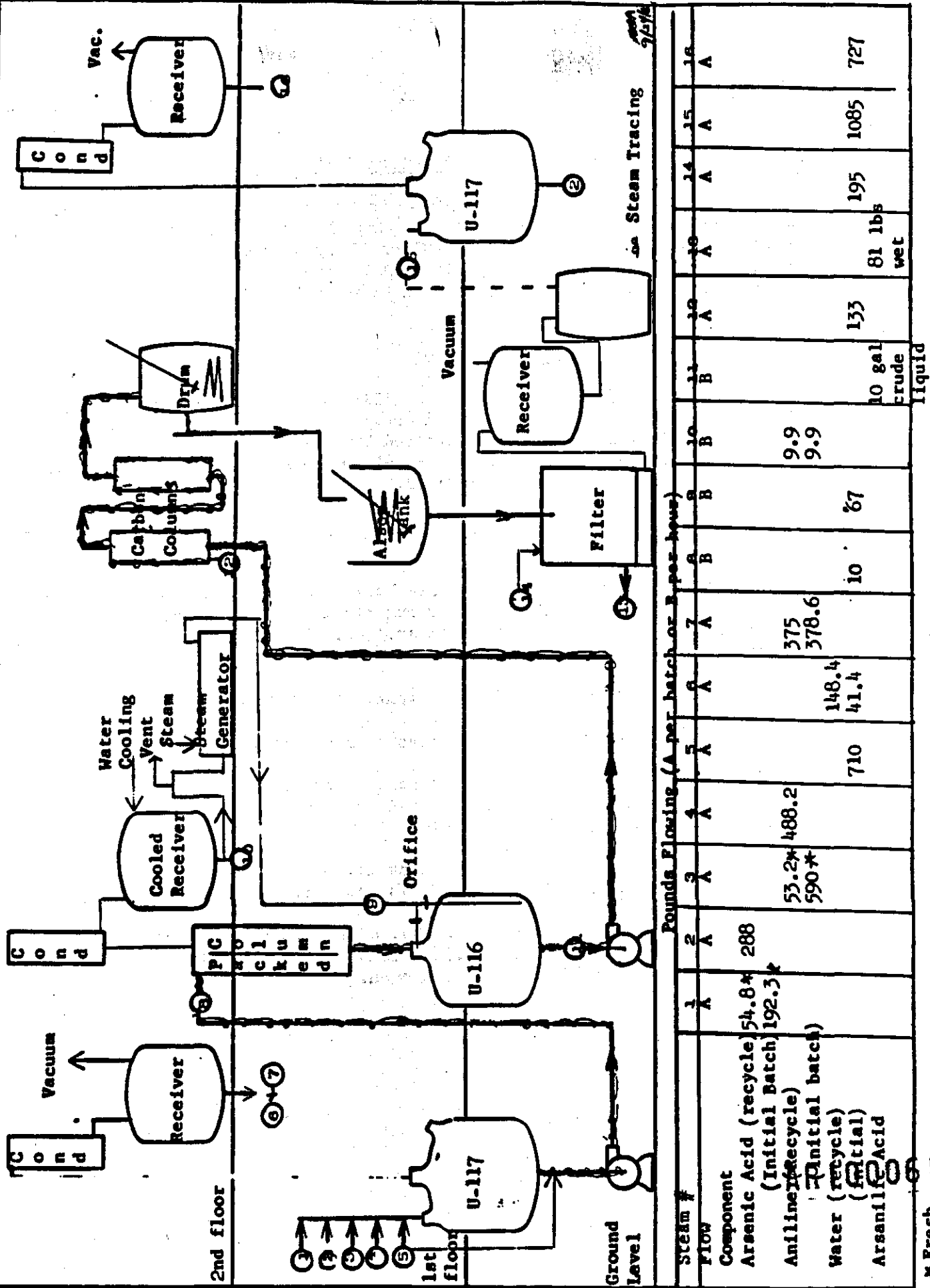
Unit 116, a 100 gallon, glass-lined kettle with a 6-inch diameter column packed with 5 feet of 1/2-inch Intalox saddles, a condenser, a cooled receiver, and a dip-pipe for part of the steam will be used for steam stripping. A heat exchanger will be used for generating steam from the aqueous layer of the aniline-water azeotrope. Unit 116 itself will act as a 2 hour surge to allow completion of the steam stripping.

#### C. Carbon-Treatment Unit

Two columns, each being 8 inches in diameter and 28 inches in length and fabricated from 316 stainless steel pipe, are to serve as carbon treating units. Each column will be packed with 7.4 lbs. of granular Nuchar C-190 carbon (Density 9.17 lbs./ft.<sup>3</sup>) Steam-stripped effluent from Unit 116 will be pumped continuously through the columns joined in series. It is expected that one batch of material from Unit 117 will exhaust the initial carbon column. Subsequent attempted carbon regeneration is a batch operation.

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**Figure 1 - Arsanilic Acid Equipment and Flow Sheet for Semi-Works**



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## D. Crystallization and Filtration Unit

An agitated vessel at 50°C. is to receive the carbon-treated stream. The container will be filled and the partially crystallized arsanilic acid permitted to flow over into a 50-gallon Alsop tank at 20°C. After a 2 hour residence time, the arsanilic acid will be separated from the mother liquor in a filter box. The crystals are to be washed batchwise.

## E. Mother Liquor Concentrator

Mother liquor from the arsanilic acid will be removed by vacuum to double thickness polyethylene-lined drums and stored until Unit 117 is empty. This material will then be concentrated by normal vacuum distillation. The bottoms are to be dropped out of the kettle into double thickness polyethylene-lined drums and stored until recycled.

## III. Reaction Charge

The charge listed below are based on the production of 65 lbs. (0.299 moles) of arsanilic acid per run starting with an initial run in one case and a follow-up recycle in another. The following conditions are assumed:

- 1.) A 5.5/1 aniline to arsenic mole ratio.
- 2.) 26% conversion of arsenic to arsanilic acid.
- 3.) 2.5% unrecoverable arsenic loss overall making the product yield 90% based on fresh arsenic required to give the desired mole ratio on recycle.
- 4.) Approximate 1.6% aniline loss overall making the product yield 75% based on fresh aniline.
- 5.) The recovery of 288 lbs. of recyclable arsenic concentrate which contains 60.6% solids having a total arsenic analysis of 21.4% and 3.0% nitrogen.

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## A. Charge For Initial Run

Whitmover Arsenic Acid - 192.3 lbs., 85%, 17.86 lbs./gal., 1.152 moles { 163.5 lbs. Acid  
28.8 lbs. H<sub>2</sub>O

Whitmover Aniline - 590.0 lbs., 100%, 8.53 lbs./gal., 6.336 moles

Total Charge - 782.3 lbs. = 80 gals. at 25°C.

## B. Charge for 1st Recycle Run

Fresh Arsenic Acid - 54.8 lbs., 85%, - - - 0.328 moles { 46.6 lbs. Acid  
8.2 lbs. H<sub>2</sub>O

Arsenic Concentrate - 288.0 lbs. { 21.4% As - - - 0.824 moles }  
(11.71 lbs./gal. at 25°C.) { Total 1.152 moles } 117.0 lbs. Acid  
(11.32 lbs./gal. at 80°C.) { 3.0% N - 0.617 moles } 113.5 lbs. H<sub>2</sub>O  
57.5 lbs. Aniline

Wet Recycle Aniline - 488.2 lbs. 98.2% - 5.148 moles  
(composite)

\* Fresh Aniline - 53.2 lbs. 100% - 0.571 moles

Total Charge 884.2 = 91 gals. at 25°C. 6.336 moles

\*  
Based on the procedure outlined, aniline in the water layer collected during the reaction step (.016 moles), aniline in an assumed 200 lb. water-layer heel which is believed necessary to promote good aniline separation during steam stripping (0.79 moles), and aniline in the water distillate resulting from the arsenic concentration step (.019 mole) would not be accountable in the system until the 2nd recycle run. This is the reason the fresh aniline charge in the 1st recycle charge appears higher than is warranted by the anticipated 75% yield based on aniline.

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## IV. Procedure

### A. Reaction Step

1. Inert Unit 117 by evacuating and filling with nitrogen; repeating several times.
2. Pump the aniline charge into the kettle as rapidly as possible.
3. With full heat applied and the agitator on, raise the batch temperature to 115-120°C.
4. Under total take-off conditions, pump the acid charge into the reactor with the temperature at 115-140°C., steam heat and 1/2 hour (0.36 gal./min.) will probably be required. Note 1.
5. After adding the acid, raise the batch temperature to 160-165°C, and maintain for 2 hours. Note Table I for distillate removal.
6. Upon completing the reaction period, remove distillate from the receiver, separating and weighing the water (upper) and aniline layers. Hold the layers for further processing (See Table I for approximate weights).

Table I - Distillate Removal During Reaction

	<u>Initial Run</u>		<u>1st Recycle Run</u>	
	<u>lbs.</u> <u>H<sub>2</sub>O</u>	<u>lbs.</u> <u>Aniline</u>	<u>lbs.</u> <u>H<sub>2</sub>O</u>	<u>lbs.</u> <u>Aniline</u>
Distillate To 160°C.	* 30	6.4	137.0	30.4
Distillate During 2 Hr. Hold	11.4	15.6	11.4	15.6
Total Distillate, lbs.		63.4		193.1
Total Aniline Removed, Moles		0.24		0.537
Aniline/Arsenic Mole Ratio After Reaction Period		5.28/1		5.04/1

\* Water layers contain 3.7% aniline. Aniline layers contain 5% H<sub>2</sub>O.

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B. Vacuum Strip Step

7. Cool the batch to 140°C. and, with continued agitation, apply gradual vacuum. When the pot temperature reaches 100°C., apply steam heat and remove aniline as rapidly as possible with the temperature at 95-100°C. Continue heating, reducing the pressure, and removing aniline until the batch temperature reaches 100°C. and the pressure reaches 30 mm of Hg. Note 2.
8. When the batch reaches 100°C. at 30 mm., discontinue heating and raise the pressure to atmospheric with nitrogen.
9. Weigh aniline distillate and hold for further processing. Note 3.
10. Place the system under total reflux and add 600 lbs. of water at 60-70°C. With continued agitation, adjust the batch temperature to 85-90°C. The adjusted batch amounts to about 967 lbs. and is equivalent to about 110 gallons (S.G. 1.065 at 90°C.). Note 4

C. Steam Stripping Step

11. Pump crude from step 10 into the steam stripper at the rate of 10 gals./hr. Simultaneous to this, pump additional dilution water (80-90°C.) at the rate of 10 lbs./hr. into the crude feed prior to the steam stripper.
12. Adjust steam rate to the base of the steam stripping column to approximately 40 lbs./hr. and 27 lbs./hr. to the dip pipe in the stripped product receiver (Unit 116, Figure 1). Note 5.
13. Allow a heel to build-up for 2 hours in the stripped product receiver before starting to pass stripped product through the carbon beds. Continue passing steam into the stripped product receiver for 20 minutes or longer after completing the addition of crude feed to the steam stripping column.
14. Separate and weigh the aniline layer (bottom) in the steam distillate receiver. Anticipated aniline recovery is 113 lbs. (100% basis). Aniline to arsenic mole ratio in the batch at this point is 0.94/1. Note 6.
15. Combine aniline recovered in Sections A, B, and C and hold for recycle. The composite is about 98% aniline and 2% H<sub>2</sub>O.

D. Carbon Treatment Step

16. After a 2 hr. build-up of stripped crude in the stripped crude receiver, start pumping steam stripped crude through the water filled carbon columns (Column Temperature 85-90°C.) at the rate of 10 gal./hr. Anticipated contact time is approximately 34 minutes in each column (Volume of each column 5.69 gal.). Anticipated pumping time 11 hours. Note 7.

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17. Pump 16 gallons of fresh (90°C.) water through the columns at 10 gals./hr. to remove the arsanilic acid after treatment of stripped crude is complete.

E. Crystallization Step

18. Collect carbon treated effluent in a 50 gallon agitated drum maintained at 50°C.
19. Allow treated effluent to build-up and overflow into an Alsop continuous crystallizer where it is finally cooled to 20°C.
20. Draw the resulting slurry off continuously and filter using a filter box. The resulting wet cake weighs about 81 lbs. (80% solids).
21. Wash the wet cake in the filter box with 65 lbs. of city water and repeat this procedure two additional times. Hold water washes for recycle as make-up water in step 10.
22. Washed wet cake weighs about 81 lbs., 80% solids. Send an aliquote sample of wet cake to Laboratory 28 for drying. Note 8.

F. Arsenic Residue Recovery Step

23. Concentrate mother liquor filtrate from step 20 (1015 lbs., 117 gals., S.G. 1.04 at 25°C.) at 90 mm until 727 lbs. (87 gals.) of distillate is removed.
24. The resulting residue should weigh 288 lbs. and contain 60.6% solids. Note 9.

G. Carbon Column Regeneration Step (Initial Run)

25. Pump 43 lbs. (S.G. 0.908 at 25°C.) of dimethylformamide into the drained initial carbon column and allow to stand 3/4 hour at 95-100°C.
26. Drain the column and repeat.
27. Fill the column with hot water and allow to stand 20 minutes. Drain and combine the effluents with the DMF solvent washes.
28. Finally fill the regenerated column with fresh water.
29. Straight-lead distill the solvent-water wash composite, removing first the water, then the dimethylformamide. Final pot temperature is 100°C. at 15 mm. This results in a slightly viscous, purple, still-bottom, arsenic-containing residue that weighs about 5 lbs. Solvent recovery is better than 88%. Note 10.

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Note 1

Allow residual water to flash off under total take-off during addition. In recycle runs, precede arsenic concentrate addition by the required fresh acid. Add concentrate at about 0.31 gal./min. Total acid-arsenic concentrate addition time should be about 1½ hours.

Note 2

Cooling the batch below 95°C. results in a tendency for the batch to solidify. Operating at a pot temperature higher than 100°C., particularly after most of the excess aniline has been removed causes the batch to darken. Reducing the aniline to arsenic mole ratio below 2/1 causes the batch to thicken and with continued removal causes precipitation.

Note 3

Anticipated aniline distillate for the initial run is 356.6 lbs. (1% H<sub>2</sub>O, 3.79 moles); for a recycle run 329 lbs. (3.5 moles). The amount of aniline removed in this step depends upon the amount of aniline removed in the reaction stage. Total aniline removed to this point, including all aniline resulting from the reaction step amounts to 375 lbs. (100% basis). Aniline to arsenic mole ratio of the batch at this point is 2/1.

Note 4

Dilution water is made up of reaction water and concentrator water when available. It might be advantageous to preheat this water to about 60°C. before addition. Concentrator water can also be used as make-up water to the vaporizer during steam stripping.

Note 5

On the initial run, feed fresh water to the vaporizer until enough aniline saturated water layer is formed (about 200 lbs.) so it can be recycled. Steam ratio to anticipated amount of aniline to be removed is about 6.5/1 based on recycle of aniline saturated water layer to the vaporizer.

Note 6

On the initial run, about .079 moles of aniline would remain in the anticipated 200 lbs. residual water layer. With continued recycle, this loss would become negligible.

Note 7

Crystallization of arsanilic acid on the carbon is possible if the bed temperature is allowed to drop below 80°C. Above 95°C. up to 100°C. the bed tends to percolate.

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Note 8

Typical Bristol analysis of dry product is as follows:

35.4% As, 6.46% N; Theory 34.51% As, 6.45% N.

Samples of dry material are also sent to Laboratory 12 for % arsenite and arsenate. These analysis usually run well below 0.025 and 0.05 respectively, which meets FDA specifications.

Note 9

Concentrate assay will vary slightly from run to run depending on the degree of concentration, efficiency of product removal from mother liquor, and how efficiently the aniline salt is steam split. The analysis usually is as follows: % Arsenic 20-22, % Nitrogen 2.9-3.1.

Note 10

The still-bottom residue, along with eventual exhausted carbon from the carbon columns, would require appropriate disposal. It may be possible that on a larger scale the carbon columns will not be regenerated satisfactorily with the treatment prescribed and/or it may not be economical. These were the best conditions found for regeneration on a laboratory scale.

V. Discussion

In addition to the desired reaction between aniline and arsenic acid to form arsanilic acid, there is some tendency for an oxidation-reduction, by-product reaction to occur. As a result of this, aniline dye and tarry by-products form. At the same time pentavalent arsenic is reduced to the tri-valent form. The latter form is inactive when recycled as part of the arsenic residue and, therefore, tends to build-up with continued recycle. This is not the case with the aniline by-products since these are removed by the carbon treatment. The rate at which the by-product reaction occurs appears to be influenced by reaction temperature and time, and amount of aniline in the charge. Oxidation occurs most rapidly as the reaction temperature is raised above 165°C. and/or as the aniline to arsenic mole ratio becomes less than 3/1. The desired arsanilic acid reaction proceeds until an approximate 25-30% arsenic conversion to arsanilic acid occurs. This may be related to the fact that arsenic acid dehydrates at an elevated temperature. Oxidation, on the other hand, appears to continue. Arsanilic acid formation occurs at a reaction temperature of 150°C., but at slower rate (doubled reaction time) than at 160-165°C. Unfortunately, the same amount of oxidation by-products appear to form during the extended reaction time as is formed at 160-165°C. with a 2 hour reaction time.

A slight advantage as regards by-product formation appears possible using a larger excess of aniline (up to a 5/1 mole ratio, aniline to arsenic). Also, charging all reactants at a temperature below 150°C. and then heating to reaction temperature appears to result in less by-product formation than is the case when arsenic is added to aniline at reaction temperature. In one laboratory

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recycle series following the latter method, arsenite-arsenic build-up rate was about 0.7% based on total arsenic charged. In this case, after completing five recycles and assuming no correction for arsenite-arsenic in recycle arsenic concentrate, product yield dropped from 26 to 15%. Conversions of two other recycle series (3.5/1 and 5.5/1) currently underway in the laboratory, in which the reactants are charged below 150°C. and heated to 160-165°C., continue above 25% after three recycles. Analytical data concerning arsenite build-up is still pending.

Preliminary data indicate that it is possible to oxidize the arsenite in a simulated arsenic concentrate by treating with hydrogen peroxide. The effect of using treated concentrate in an arsenation has not as yet been tried.

Another by-product known to form in the arsanilic reaction is diamino-diphenyl arsonic acid (approx. 1.5% based on total arsenic). In the Whitmoyer process this material is recovered during a fractional precipitation step by pH adjustment. It is not isolated in the Laboratory 28 process. Thin layer chromatography of the carbon used in decolorizing reaction product indicates the presence of DDAA; however, the amount of this material present appears much less than is indicated in Whitmoyer's isolation procedure. It is possible that this material may hydrolyze during the steam stripping step. Experiments are planned to show if this possibility exists.

The closeness of the densities of aniline and water (aniline being slightly heavier at 25°C.) results in a slightly sluggish layer separation. To further complicate the situation, the layers invert at 80-90°C. In the proposed process, it is assumed that if steam distillate is allowed to condense and is collected in a receiver at about 25°C., layer separation will be efficient enough, with a 200 lb. water layer build-up, to recycle the top water layer to the vaporizer. Aniline-saturated water layer has been satisfactorily recycled in the laboratory, but no attempt has been made to do this on a continuous basis.

Solvent extraction has been successfully tried (batchwise) to recover aniline from saturated water layer. With three extractions, using 1 part benzene to 13 parts water layer, 89% of the residual aniline was recovered; aniline content in the water layer being reduced from 3.7% to < 0.2%.

An extensive investigation with different types of carbon for the treatment of crude stripped reaction product has not been carried out. Of the two carbons tried (Nuchar C-190, 30 mesh, West Virginia Pulp and Paper Co.; Cal-Type, 30 mesh, Pittsburgh Coke and Chem. Co.), Nuchar C-190 appeared to decolorize most efficiently (6 lbs. arsanilic produced/lb. carbon) and is cheaper (12.5¢ lb.).

Arsanilic acid resulting from the Laboratory 28 process is crystalline in nature as compared to the powdery material isolated by Whitmoyer. Other than for the manufacture of Carbarsone (cyanate derivative of arsanilic acid), arsanilic acid is dried before blending or packaging. It appears that the drying process should be fairly mild (50°C. max. at 90 mm.). In most cases

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laboratory acid samples were dried 8 hours in an 80°C. oven at atmospheric pressure. Arsenic and nitrogen assays for arsenic and nitrogen were slightly higher than theory for arsanilic. Thin layer chromatography and wet chemical analysis did not indicate impurities other than trace amounts of arsenate and arsenite. It is believed that under the drying conditions used partial dehydration occurred. An attempt will be made to determine if this is the case.

In most of our work, CO<sub>2</sub> has been employed to maintain the system oxygen-free. However, we have not been able to demonstrate any beneficial effect of CO<sub>2</sub> on the actual reaction other than to possibly minimize oxidation. Accordingly, for the Semi-Works study we have agreed to the use of nitrogen to inert the system initially. The use of nitrogen in place of CO<sub>2</sub> is more convenient in the reaction area.

H. R. Raterink

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S. Wise

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D. Nicodemus

D. Nicodemus

HR:SW:DN:PAH

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